

## CLAIMS

## WHAT IS CLAIMED IS:

1. A method for solid free-form fabrication of a three-dimensional object, comprising:  
depositing a particulate blend in a defined region, said particulate blend including reactive glass ionomer particulates, cross-linkable polyacid particulates including polyvinyl pyrrolidone-co-polyacrylic acid, and nanocomposites;  
ink-jetting an aqueous phase binder onto a predetermined area of said particulate blend to form hydrated cement in said predetermined area; and  
hardening said hydrated cement.
2. The method of claim 1, further comprising removing a portion of said particulate blend that does not form said hydrated cement.
3. The method of claim 1, wherein said reactive glass ionomer particulates comprise a glass ionomer cement.
4. The method of claim 1, wherein said cross-linkable polyacid particulates comprise a polyvinyl pyrrolidone-co-polyacrylic acid and one of a polyacrylic acid, a polygalaturonic acid, a polyethelyne-co-maleic acid.
5. The method of claim 1, wherein said nanocomposites comprise one of PEO/clay nanocomposites, closite 10A, closite 30B, closite Na<sup>+</sup>, hydrophilic polymer-silicate nanocomposites, hydroxyapatite nanocomposites, or layered double hydroxide (LDH) nanocomposites.
6. The method of claim 1, wherein said particulate blend further comprises a source of Al<sup>3+</sup>.

7. The method of claim 1, wherein said particulate blend further comprises a source of  $\text{Zn}^{2+}$ .
8. The method of claim 1, wherein said particulate blend further comprises biomolecules.
9. The method of claim 8, wherein said biomolecules comprise dextrin or soluble starch.
10. The method of claim 1, wherein said particulate blend further comprises a nanofiller.
11. The method of claim 10, wherein said nanofiller comprises hydroxyapatite.
12. The method of claim 1, wherein said step of hardening said cement is accelerated by including a pH modifier in said particulate blend.
13. The method of claim 12, wherein said pH modifier comprises one of tartaric acid, citric acid, glutamic acid, diglycolic acid, DL aspartic acid, iminodiacetic acid, itaconic acid, or  $\text{NH}_4\text{H}_2\text{PO}_4$ .
14. The method of claim 1, wherein said aqueous binder comprises a pH modifier to accelerate hardening said cement.
15. The method of claim 14, wherein said pH modifier comprises one of phosphoric acid, phytic acid or citric acid.
16. The method of claim 1, wherein said aqueous binder comprises colorants.

17. The method of claim 1, wherein said aqueous binder comprises phytic acid, citric acid, dye colorants, pigment colorants, pyrrolidone, 1,5-hexanediol, low molecular weight water-soluble ethylene oxide-propylene oxide oligomers, surfynol 465, and water.

18. A system for SFF of three-dimensional objects comprising:  
a particulate blend including reactive glass ionomer particulates, cross-linkable polyacid particulates including polyvinyl pyrrolidone-co-polyacrylic acid, and nanocomposites; and  
an ink-jettable aqueous binder configured to hydrate said particulate blend to form a cement.

19. The system of claim 18, wherein said reactive glass ionomer particulates comprise a glass ionomer cement.

20. The system of claim 18, wherein said cross-linkable polyacid particulates comprise a polyvinyl pyrrolidone-co-polyacrylic acid and one of a polyacrylic acid, a polygalaturonic acid, a polyethelyne-co-maleic acid.

21. The system of claim 18, wherein said nanocomposites comprise one of PEO/clay nanocomposites, closite 10A, closite 30B, closite Na<sup>+</sup>, hydrophilic polymer-silicate nanocomposites, hydroxyapatite nanocomposites, or layered double hydroxide (LDH) nanocomposites.

22. The system of claim 18, wherein said particulate blend further comprises a source of Al<sup>3+</sup>.

23. The system of claim 18, wherein said particulate blend further comprises a source of Zn<sup>2+</sup>.

24. The system of claim 18, wherein said particulate blend further comprises biomolecules.

25. The system of claim 24, wherein said biomolecules comprise dextrin or soluble starch.

26. The system of claim 18, wherein said particulate blend further comprises a nanofiller.

27. The system of claim 26, wherein said nanofiller comprises hydroxyapatite.

28. The system of claim 18, wherein said particulate blend further comprises a pH modifier.

29. The system of claim 28, wherein said pH modifier comprises one of tartaric acid, citric acid, glutamic acid, diglycolic acid, DL aspartic acid, iminodiacetic acid, itaconic acid, or  $\text{NH}_4\text{H}_2\text{PO}_4$ .

30. The system of claim 18, further comprising an ink-jet material dispenser configured to selectively jet said ink-jetable aqueous binder onto said particulate blend.

31. The system of claim 18, further comprising a substrate configured to carry said particulate blend in a defined region, said defined region being configured with respect to said ink-jet material dispenser such that said ink-jetable aqueous binder, upon being ink-jetted from said ink-jet material dispenser, contacts said particulate blend.

32. The system of claim 18, wherein said system is configured to form multiple layers of cement such that each layer of said cement is bound to at least one adjacent layer.

33. The system of claim 18, wherein said particulate blend comprises 75 wt% reactive glass, 10 wt% polyacrylic acid (PAA) (MW 60K), 5 wt% tartaric acid, 2.5 wt% citric acid, 2.5 wt% polyethylene oxide (PEO)/clay nanocomposites, and 5 wt%  $\text{Al}(\text{NO}_3)_3$ .

34. The system of claim 18, wherein said particulate blend comprises 80 wt% reactive glass, 5 wt% PAA (MW 60K), 5 wt% glutamic acid, 2.5 wt% diglycolic acid, 2.5 wt% polyethylene oxide (PEO)/clay nanocomposites, and 5 wt% Dextrin.

35. The system of claim 18, wherein said particulate blend comprises 75 wt% reactive glass, 10 wt% polygalaturonic acid, 5 wt% DL aspartic acid, 2.5 wt% citric acid, 2.5 wt% polyethylene oxide (PEO)/clay nanocomposites, and 5 wt% hydroxyapatite.

36. The system of claim 18, wherein said particulate blend comprises 70 wt% reactive glass, 10 wt% zinc oxide (ZnO), 10 wt% PE-co-maleic acid, 3 wt% citric acid, 3 wt% iminodiacetic acid, 2 wt% soluble starch, and 2 wt% Closite 10A.

37. The system of claim 18, wherein said particulate blend comprises 60 wt% reactive glass, 20 wt%  $(\text{NH}_4)\text{H}_2\text{PO}_4$ , 5 wt% PAA (MW 60K), 5 wt% polygalaturonic acid, 5 wt% iminodiacetic acid, and 5 wt% Closite 10A.

38. The system of claim 18, wherein said particulate blend comprises 75 wt% reactive glass, 8 wt% itaconic acid, 10 wt% PE-co-maleic acid, 2 wt% citric acid, 2 wt% soluble starch, and 3 wt% Closite 30B.

39. The system of claim 18, wherein said particulate blend comprises 75 wt% reactive glass, 10 wt% polyvinyl pyrrolidone-co-polyacrylic acid (PVP-co-PAA), 8 wt% itaconic acid, 3 wt% Closite Na<sup>+</sup>, 2 wt% citric acid, and 2 wt% soluble starch.

40. The system of claim 18, wherein said particulate blend comprises 75 wt% reactive glass, 8 wt% itaconic acid, 10 wt% PVP-co-PAA, 2 wt% citric acid, 2 wt% soluble starch, and 3 wt% Closite 30B.

41. The system of claim 18, wherein said ink-jetable aqueous binder comprises a colorant.

42. The system of claim 18, wherein said ink-jetable aqueous binder comprises components configured to improve jettability of said ink-jetable aqueous binder, said components including water and surfactants.

43. A solid three-dimensional prototype composition, comprising:  
multiple layers of cement deposited in contact with one another, each of said multiple layers of cement comprising a particulate blend including reactive glass ionomer particulates, cross-linkable polyacid particulates including polyvinyl pyrrolidone-co-polyacrylic acid, and nanocomposites;  
wherein said particulate blend was hydrated and hardened by use of an ink-jetable aqueous binder.

44. The composition of claim 43, wherein said nanocomposites further comprise one of PEO/clay nanocomposites, closite 10A, closite 30B, closite Na<sup>+</sup>, hydrophilic polymer-silicate nanocomposites, hydroxyapatite nanocomposites, or layered double hydroxide (LDH) nanocomposites.

45. The composition of claim 43, wherein said multiple layers of cement further comprises biomolecules.

46. The composition of claim 43, wherein said multiple layers of cement further comprises a pH modifier.

47. The composition of claim 46, wherein said pH modifier comprises one of tartaric acid, citric acid, glutamic acid, diglycolic acid, DL aspartic acid, iminodiacetic acid, itaconic acid, or  $\text{NH}_4\text{H}_2\text{PO}_4$ .

48. The composition of claim 43, wherein said composition further comprises a colorant.